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CONTRIBUTIONS FROM THE LABORATORY OF THE UNIVERSITY OF  
PENNSYLVANIA.

## No. IX.

*Upon some new Chlorine Derivatives from Toluol.*

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The first of these derivatives which it is my intention to describe in the following lines was obtained by me some time ago, and also a description of it published (Inaugural Dissertation, Göttingen, 1876), but as it is intimately connected with the subsequent work a brief description of its production and properties may probably not be amiss.

## PRODUCTION OF TOLUOLTRICHLORIDE OR BENZYLTRICHLORIDE.

This was obtained in the usual manner, viz.: By the introduction of a calculated amount of dry chlorine into boiling Toluol. The liquid boiling at  $218^{\circ}$  C. was collected and treated as follows :

FORMATION OF  $C_{21}Cl_{26}$ .

The pure Benzyltrichloride was placed in a large flask and dried chlorine gas conducted into the liquid until it was no longer absorbed and the vacant space also filled with it, when the flask was tightly corked and exposed to the action of the sun-light. After standing a few days the green color of the chlorine had disappeared. The flask was again filled with the gas and this operation repeated, until the chlorine was apparently no longer absorbed. The flask was now set in a rather cool place and allowed to remain there for some time. After standing several months I noticed that crystals had separated from the liquid. These were immediately brought upon a filter, washed thoroughly with water and then pressed between filter paper to remove any Benzyltrichloride that may have adhered to the crystal mass. After drying the compound by exposure to the air, it was pulverized and dissolved in chloroform, from which solution it crystallized in fine, colorless crystals, which after repeated re-crystallization fused at  $152^{\circ}$ – $153^{\circ}$  C.

*Properties.*—The compound possesses an odor very similar to that of camphor, is insoluble in water and alcohol, but readily soluble in chloroform. It is volatile without decomposition. My attempts to affect the introduction of the  $NO_2$  group were unsuccessful. Even with the aid of heat nitric acid is without any action.

If the compound is allowed to crystallize slowly from a chloroform solution, crystals may be obtained half an inch long and one-fourth of an inch broad. These have prism and dome faces.

I never succeeded in obtaining the compound during summer, very probably because the Benzyltrichloride held it in solution.

Numerous analyses made of the compound lead to the following formula :  $C_{21}Cl_{26} = (C_6Cl_6C_3Cl_3)_3$ . ( $C_6Cl_5C_3Cl_3$ ). ( $C_6Cl_6C_3Cl_3$ ).

We have here, then, a compound in which three benzol groups have very probably combined, containing only carbon and chlorine.

#### ANALYSES.

##### *Chlorine Determinations.*

I. The compound was dried over sulphuric acid and burned with oxide of lime, and the calcium chloride which was produced dissolved in nitric acid and the chlorine precipitated with silver nitrate.

0.2181 Grm. substance gave .6928 Grm. silver chloride, corresponding to 78.53 % chlorine.

II. .1035 Grm. substance gave .329 Grm. silver chloride = 78.58 % chlorine.

III. 0.0868 Grm. substance gave .2765 Grm.  $\text{AgCl}$  = 78.57 % chlorine.

IV. Finally, I fused a portion of the compound on a watch glass and then heated it with oxide of lime.

.0893 Grm. sub. gave .2843 Grm. silver chloride = 78.75 % chlorine.

##### *Carbon Determinations.*

I. .3629 Grm. substance dried at  $75^{\circ}\text{C}$ . and then burned with coarse lead chromate, yielded .0780 Grm.  $\text{CO}_2$  = 21.41 % carbon.

Not any water was noticed in the calcium chloride tube and its weight had not increased.

II. .2513 Grm. dried substance, burnt with lead chromate gave .0536 Grm.  $\text{CO}_2$  = 21.33 % carbon.

III. .1677 Grm. well dried substance gave .0361 Grm.  $\text{CO}_2$  = 21.51 % carbon.

Several more combustions were made with about the same result. In no instance did the found percentage of water exceed 0.40 %. This amount of moisture could have readily collected during the filling of the combustion tube.

#### RESULTS.

Calculated.	Found.
$\text{C}_{21} = 252 = 21.44\%$	21.41 — 21.33 — 21.51
$\text{Cl}_{26} = 923 = 78.56\%$	78.57 — 78.58 — 78.53 — 78.75.

##### ACTION OF ZINC AND SULPHURIC ACID UPON $\text{C}_{21}\text{Cl}_{26}$ .

About five grammes of the preceding compound were pulverized and dissolved in a mixture of alcohol and chloroform, and zinc and sulphuric acid added to this solution. The liberation of hydrogen gas was rather slow and to hasten it the flask containing the mixture was placed on a sand-bath, where a constant temperature of  $60^{\circ}\text{C}$ . was maintained for ten weeks, during which period there was a constant and brisk disengagement of hydrogen gas. The flask was now placed upon a water-bath and the alcohol and chloroform removed by distillation. An impure oil remained as a residue and upon cooling solidified and was then taken from the flask and dissolved in a mixture of chloroform and alcohol. After removing the impurities by filtration, the solution was strongly evaporated and when cool the compound separated partly as an oil and partly in colorless tablets.

After pouring off the supernatant liquid the crystalline mass was pressed well between filter paper and then dissolved in alcohol. From this solution the compound crystallized in beautiful, colorless, quadratic plates, which after several recrystallizations fused at  $102^{\circ}\text{C}$ .

*Properties.* If a crystal is fused upon a piece of glass it will remain in a plastic condition for hours and stirring it with the point of a knife blade will not cause solidification. One crystal which I fused required twelve hours before becoming solid. The fusing point of this solidified mass was the same as that of the crystals,  $102^{\circ}\text{C}$ .

The compound may be volatilized without suffering decomposition. When pure it possesses a very peculiar, aromatic odor, somewhat like that of the preceding compound, being only more piercing.

The compound is perfectly insoluble in water, but very readily soluble in chloroform. The best solvent I found to be alcohol, in which, when warm, it is exceedingly soluble.

The following analyses were made :

*Chlorine Determination.*

0.4180 Grm. substance dried over calcium chloride and burned with oxide of lime gave 1.3146 Grm. silver chloride = .3252 Grm. chlorine = 77.79 % chlorine.

*Carbon Determination.*

.3812 Grm. air dried substance burned with lead chromate, gave 21.69 % carbon and 1.00 % hydrogen.

If we suppose that only one hydrogen atom has replaced chlorine, the following numbers would be required :

Calculated.	Found.
$\text{C}_{21} = 22.09\%$	21.69 %
$\text{Cl}_{25} = 77.81\%$	77.79 %
$\text{H} = 0.09\%$	1.0 %

The formula would, therefore, be  $\text{C}_{21}\text{Cl}_{25}\text{H}$ . That the replacement would be so very limited, one would naturally suppose if he considered the presence of such a large number of negative chlorine atoms.

ACTION OF SODIUM AMALGAM UPON  $\text{C}_{21}\text{Cl}_{25}\text{H}$ .

The substance was finally divided and dissolved in an excess of alcohol, and sodium amalgam added to the solution. The liberation of hydrogen gas was at first very violent, finally, however, the application of heat upon a sand bath was necessary to render the disengagement continuous. After allowing the action to continue three or four days, I interrupted it and proceeded to examine the contents of the flask.

The alcohol was distilled off, and as the liquid gradually diminished in volume, drops of oil separated from it. Only a small quantity of the oil could be obtained, and after being purified, was too small to employ in an analysis, expected to afford some clue to the composition of the compound. Intense cold would not render this oil solid.

ACTION OF SODIUM AMALGAM UPON  $C_{21}Cl_{26}$ .

Ten grammes of the substance were reduced to a powder, placed in a small flask, and alcohol then poured in, and the whole heated upon a sand bath for four weeks. At the expiration of this time the alcoholic solution was poured off from the metallic mercury that had collected upon the bottom of the flask, and water and hydrochloric acid added to the solution to dilute it and neutralize any sodium carbonate that may have formed.

Upon adding the water I noticed the appearance of oil globules, which swam upon the surface of the liquid.

The solution was placed in a suitable vessel and subjected to distillation upon a water bath. In the receiver a rather large quantity of oil collected. In the flask, upon examination, I found merely sodium chloride.

The further addition of water to the liquid in the receiver rendered it cloudy, and it was again distilled, but this time over a free flame. The alcohol, of course, first passed over, and the addition of water to it produced no cloudiness.

The oil was carried over with the steam and collected to one large globule on the bottom of the receiver.

Soon after all the oil had passed over, I noticed the liquid carried over small shining needles. The receiver was immediately changed and the distillation continued. Only a small quantity of this crystallized compound was caught. It was exceedingly soluble. It was extracted from its aqueous solution with ether and the latter allowed to evaporate. The residue consisted of fine colorless needles, possessing a rather sharp odor. The compound fused at about  $127^{\circ} C.$  With barium carbonate it gave a salt crystallizing in white needles. Scarcity of material prevented its analysis.

To extract the oil from the aqueous solution ether was added, and the two liquids separated with a separatory funnel. After the evaporation of the ether, the oil was treated with calcium chloride, to remove any adherent moisture and afterwards dried over sulphuric acid.

*Properties.* The oil is perfectly clear. Insoluble in water, but soluble in ether. It is with difficulty volatilized.

The following analyses were made :

*Carbon Determination.*

.1132 Grm. of the oil were placed in a small bulb tube and burned with lead chromate, yielding .1603 Grm.  $CO_2 = .043\%$  Carbon = 38.60% further, .0500 water = .0056 H = 4.94% H.

Upon examining the bulb tube after the combustion, a small quantity of undecomposed carbon was noticed.

*Chlorine Determination.*

.0463 Grm. oil ignited with oxide of lime gave .0980 Grm. silver chloride — 52.33 % chlorine.

## RESULT.

C = 38.60%

Cl = 52.33%

H = 4.94%